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Application Identifier : Christopher J. Warren, et al.
Title : COMBINATORIAL ELECTROCHEMICAL
DEPOSITION AND TESTING SYSTEM
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By:

Melissa Hardy

Santa Clara, California
July 20, 1998

Assistant Commissioner for Patents
Box Patent Application
Washington, D.C. 20231

UTILITY PATENT APPLICATION TRANSMITTAL

APPLICATION ELEMENTS

1. ☒ FEE

TOTAL AMOUNT OF PAYMENT: \$ 705.00

METHOD OF PAYMENT

The Commissioner is hereby authorized to charge indicated fees and credit any overpayments to:

Deposit Account Number: 50-0496

Deposit Account Name: Symyx Technologies

☒ Charge Any Additional Fee Required Under 37 CFR 1.16 and 1.17

FEE CALCULATION

BASIC FILING FEE

Large Fee Code	Entity Fee (\$)	Small Fee Code	Entity Fee (\$)	Fee Description	Fee Paid
101	790	201	395	Utility filing fee	\$395
106	330	206	165	Design filing fee	
107	540	207	270	Plant filing fee	
108	790	208	395	Reissue filing fee	
114	150	214	75	Provisional filing fee	
SUBTOTAL (1)					(\$) 395

EXTRA CLAIM FEES

Extra Claims				Fee from below		Fee Paid
Total Claims	37	-20**	=	17	X 11	= \$187
Independent Claims	6	-3**	=	3	X 41	= \$123
SUBTOTAL (2)						(\$) 310

**or number previously paid, if greater; For Reissues, see below

Large Fee Code	Entity Fee (\$)	Small Fee Code	Entity Fee (\$)	Fee Description
103	22	203	11	Claims in excess of 20
102	82	202	41	Independent claims in excess of 3
104	270	204	135	Multiple dependent claim, if not paid
109	82	209	41	**Reissue independent claims over original patent
110	22	210	11	**Reissue claims in excess of 20 and over original patent

2. ☒ Specification [Total Pages 21]
3. ☒ Drawing(s) (35 U.S.C. 113) [Total Sheets 8]
4. ☒ Oath or Declaration [Total Pages 3]
 - a. ☒ Newly executed (original or copy)
 - b. ☐ Copy from a prior application (37 C.F.R. § 1.63(d))
(for continuation/divisional with Box 17 completed) [Note Box 5 below]
 - i. ☐ DELETION OF INVENTOR(S)
Signed statement attached deleting inventor(s) named in the prior application,
see 37 C.F.R. §§ 1.63(d)(2) and 1.33 (b)
5. ☐ Incorporation By Reference (useable if Box 4b is checked)
The entire disclosure of the prior application, from which a copy of the oath or declaration is
supplied under Box 4b, is considered to be part of the disclosure of the accompanying application
and is hereby incorporated by reference therein.
6. ☐ Microfiche Computer Program (Appendix)

7. ☐ Nucleotide and/or Amino Acid Sequence Submission ☐ Computer Readable Copy
(if applicable, or necessary) ☐ Paper Copy (identical to computer copy)
☐ Stmt verifying identify of above copies

ACCOMPANYING APPLICATION PARTS

8. ☒ Assignment Papers (cover sheet and document(s))
9. ☒ 37 C.F.R. §3.73(b) Statement ☒ Power of Attorney
(when there is an assignee)
10. ☐ English Translation Document (if applicable)
11. ☒ Information Disclosure Statement (IDS)/PTO-1449 ☒ Copies of IDS Citations
12. ☐ Preliminary Amendment
13. ☒ Return Receipt Postcard (MPEP 503)
(Should be specifically itemized)
14. ☒ Small Entity Statement ☐ Statement filed in prior application,
Status still proper and desired (PTO/SB/09-12)
15. ☐ Certified Copy of Priority Document(s)
(if foreign priority is claimed)
16. ☐ Other:

*A new statement is required to be entitled to pay small entity fees, except where one has been filed in a prior application and is being relied upon.

17. **IF A CONTINUING APPLICATION**, check appropriate box, and supply the requisite information below and in a preliminary amendment:

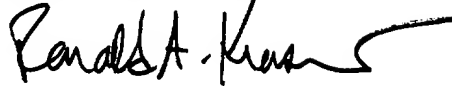
☐ Continuation ☐ Divisional ☒ Continuation-in-part (CIP) of prior application No:08/941,170

Prior application information: Examiner_____ Group/Art Unit_____

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Express Mail Label No. EI768182393US
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PATENT APPLICATION

for

**COMBINATORIAL ELECTROCHEMICAL DEPOSITION
AND TESTING SYSTEM**

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000220 2876760

5 **COMBINATORIAL ELECTROCHEMICAL DEPOSITION AND**
 TESTING SYSTEM

 This application is a continuation-in-part of U.S. patent application 08/941,170
10 filed September 30, 1997, pending, the techniques of which are incorporated herein by
reference for all purposes

 FIELD OF THE INVENTION

15 The present invention relates to methods and apparatus for the electrodeposition
of diverse materials. More specifically, the invention comprises a fully automated
electrochemical deposition and testing system for the synthesis and parallel screening of
distinct materials on arrays of individually addressable electrodes.

20 BACKGROUND OF THE INVENTION

 Among the different techniques for the preparation of metal deposits,
electrodeposition (also known as electroplating) is particularly attractive because of its
relatively inexpensive instrumentation, low temperature operation, and simplicity. A
25 further advantage of the technique is the relatively straightforward control of the
thickness and composition of the depositing layers through electrical quantities such as
current passed and potential applied.

 Electroplating has been employed in small scale as well as industrial processes.
For example, electroplating of precious metals to improve the appearance of an article or
30 to create special effects is well known. Electroplating is also employed to improve the
corrosion resistance of corrosive substances by depositing thin surface films of corrosion
resistant metals such as zinc, tin, chromium, nickel and others. Wear resistant and
friction modifying coatings of nickel, chromium, titanium and other metals and their

alloys are used to improve the wear resistance of bearing surfaces. Electroplating is also employed in the electronics industry to improve or modify the electrical properties of substrates such as contacts, printed circuits, electrical conductors, and other electrical items in which specific surface or surface-to-substrate conductive properties are desired.

- 5 Distinct metals are often electroplated onto metal surfaces to improve soldering characteristics or to facilitate subsequent coating by painting or application of other adhering films such as plastics, adhesives, rubber, or other materials.

Although the electrodeposition of a single material has been extensively studied, the deposition of two or more metals by electrochemical methods is difficult because the
10 conditions favorable for the deposition of one metal may differ substantially with those necessary for the deposition of the other. Factors including widely differing reduction potentials, internal redox reactions that can alter the oxidation states of the materials in solution, and species that are or become insoluble during the deposition can disrupt the process. Moreover, the nature of the electrodeposit itself is determined by many factors
15 including the electrolyte composition, pH, temperature and agitation, the potential applied between the electrodes, and the current density. These issues are more prevalent as the complexity of the electrodeposit (and hence the number of species in solution) increases.

Complex electrodeposited materials are desired in areas such as catalysis where
20 the composition of the electrodeposit is critical to its catalytic activity. The discovery of new catalytic materials depends largely on the ability to synthesize and analyze new compounds. Given approximately 100 elements in the periodic table that can be used to make such catalysts, and the fact that ternary, quaternary and greater compositions are desired, an incredibly large number of possible compositions is generated. Taking each
25 of the previously noted electrochemical issues into account for every possible electrodeposit and designing a synthetic strategy that can effectively cover phase space using traditional synthetic methodologies is a time consuming and laborious practice. As such, there exists a need in the art for a more efficient, economical, and systematic approach for the synthesis of novel materials and for the screening of such materials for
30 useful properties. See, for example, copending U.S. patent application 08/327,513 entitled "The Combinatorial Synthesis of Novel Materials" (published as WO 96/11878).

As an example of the utility of exploring phase space for more effective catalysts, one can consider the effect of changing the composition of the anode in a direct methanol fuel cell. A tremendous amount of research in this area has concentrated on exploring the activity of surface modified binary, and to a much lesser extent ternary, alloys of platinum in an attempt to both increase the efficiency of and reduce the amount of precious metals in the anode part of the fuel cell. Although electrodeposition was explored as a route to the synthesis of anode materials (e.g., F. Richarz et al. *Surface Science*, **1995**, 335, 361), only a few compositions were actually prepared, and these compositions were made using traditional single point electrodeposition techniques. Such an approach becomes very inefficient when exploring and optimizing new multi-component systems. Recently, Mallouk, et al. reported work on combinatorial electrochemistry as a route to fuel cell anode materials (*Science*, **1998**, 280, 1735), but this technique did not employ electrodeposition techniques.

The present invention provides a method to use electrodeposition to synthesize and evaluate large numbers of distinct materials in relatively short periods of time, significantly reducing the time consuming and laborious processes normally associated with a novel materials discovery program.

SUMMARY OF THE INVENTION

This invention provides methods and apparatus for electrochemically depositing distinct materials on arrays of individually addressable electrodes. The invention also provides a means of testing the as deposited materials for specific properties of interest.

One embodiment of the invention includes the individually addressable electrode arrays and their associated fabrication and processing steps.

Another embodiment of the invention includes an automated deposition system comprising a solution delivery head and its associated electronics and robotics. The delivery head is capable of automatically dispensing precise mixtures of plating solutions to predefined locations above the working electrodes on the individually addressable electrode arrays. The head contains a reference and counter electrode, and while delivering the plating solutions completes a circuit with a given working electrode on the

array. Adjusting the potential applied to the working electrode on the array results in the deposition of materials from the delivered plating solutions.

Another embodiment of the invention includes an electrochemical testing system comprising an electrochemical cell, a multi-channel potentiostat, and an electronic interface designed to couple the addressable array to the potentiostat such that individual electrodes on the array may be addressed, either serially or in parallel, for the measurement of a specific material property under investigation.

BRIEF DESCRIPTION OF THE DRAWINGS

In order to better understand the present invention, reference should be made to the following detailed description taken in conjunction with the accompanying drawings wherein:

FIG. 1A illustrates an array of 64 individually addressable electrodes made in accordance with the present invention;

FIG. 1B illustrates an array of 66 individually addressable electrodes made in accordance with the present invention;

FIG. 2A is a flow chart diagram describing the processes involved in fabricating individually addressable electrode arrays;

FIGS. 2A and 2B are examples of masks for array fabrication;

FIG. 3 is a sectional view of the electrochemical deposition head;

FIG. 4A is a sectional view of the electrochemical cell;

FIG. 4B is a sectional view of the cathode assembly associated with the electrochemical cell of FIG. 4A;

FIG. 4C is an exploded view of the anode assembly associated with the electrochemical cell of FIG. 4A;

FIG. 4D is a sectional view of the PCB interface associated with the anode assembly of FIG. 4C;

FIG. 4E is a circuit diagram showing the electrical connections in the PCB interface of Fig. 4D; and

FIG. 5 is a graph illustrative of the relationship between electrode composition and associated activity for an example system synthesized and measured using embodiments of the present invention.

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DETAILED DESCRIPTION OF THE INVENTION

The present invention comprises an electrochemical synthesis and testing system consisting of a number of separate parts including individually addressable electrode arrays, a fully automated deposition head, an electrochemical cell and its associated electronics, and a multi-channel potentiostat. These components provide a means for
10 investigating complex multi-component systems, by giving a user the ability to rapidly synthesize and evaluate large numbers of diverse materials in short periods of time.

The individually addressable electrode arrays 10 of the present invention are illustrated in FIGS. 1A and 1B. The arrays 10 consist of either sixty-four or sixty-six
15 independent electrodes 12 (with areas of between 1 and 2 mm²) that are fabricated on inert substrates 14. Arrays with as little as 10 or as many as 100 electrodes may be made in accordance with the methods provided in the present invention. Example substrates include, but are not limited to, glass, quartz, sapphire, alumina, plastics, or thermally treated silicon. Other suitable substrate materials will be readily apparent to those of skill
20 in the art. The individual electrodes 12 are located substantially in the center of the substrate 14, and are connected to contact pads 13 around the periphery of the substrate with wires 16. The electrodes 12, associated wires 16, and contact pads 13 are fabricated from conducting materials (such as gold, silver, platinum, copper, or other commonly used electrode materials). In a preferred embodiment of the present invention, the arrays
25 are fabricated on standard 3" thermally oxidized single crystal silicon wafers, and the electrodes are gold with surface areas of about 1.26mm².

Still referring to FIGS. 1A and 1B, a patterned insulating layer 18 covers the wires 16 and an inner portion of the peripheral contact pads 13, but leaves the electrodes and the outer portion of the peripheral contact pads exposed (preferably approximately
30 half of the contract pad is covered with this insulating layer). Because of the insulating layer 18, it is possible to connect a lead (e.g., an alligator clip) to the outer portion of a

given contact pad and address its associated electrode while the array is immersed in solution, without having to worry about reactions that can occur on the wires or peripheral contact pads. The insulating layer may be, for example, glass, silica (SiO_2), alumina (Al_2O_3), magnesium oxide (MgO), silicon nitride (Si_3N_4), boron nitride (BN), yttrium oxide (Y_2O_3), titanium dioxide (TiO_2), hardened photoresist, or other suitable material known to be insulating in nature.

Once a suitable inert substrate is provided, photolithographic techniques can be applied to design and fabricate electrode array patterns on it. By applying a predetermined amount of photoresist to the substrate, photolyzing preselected regions of the photoresist, removing those regions that have been photolyzed (e.g., by using an appropriate developer), depositing one or more metals over the entire surface and removing predetermined regions of these metals (e.g., by dissolving the underlying photoresist), one can fabricate intricate patterns of individually addressable electrodes on the substrate.

The process by which the individually addressable electrode arrays of the present invention are fabricated is described with reference to the flow chart illustrated in FIG. 2A. Starting with a cleaning step 22 that comprises washing the wafer in a suitable solvent (such as methanol or isopropanol) followed by baking in a plasma cleaning oven, a photoresist deposition step 24 in which a first layer of photoresist is applied to the wafer is then done. Although many different types of photoresist can be used for the same effect, the preferred type in the present invention is Shipley Microposit S-1813 (or equivalent). The photoresist is applied to the wafer using a standard spin coating system (commonly used and familiar to those skilled in the art) which is set to leave a final thickness of between 1 and 2 μm on the wafer. The photoresist is then cured at a predetermined temperature for a predetermined time to condition the photoresist. In a preferred embodiment of the present invention, the curing temperature is between 90°C and 130°C and the curing time is between 30 sec and 2 minutes.

A primary electrode mask 27, an example of which is shown in Fig. 2B, (which is the negative of the electrode array pattern desired) is then placed over the wafer that is then photolyzed on a mask aligner system (commonly used and familiar to those skilled in the art). After exposure to ultraviolet (UV) light during the photolysis step 26, regions

29 on the wafer are then dissolved away using an appropriate developing solution (e.g., Shipley Microposit MF-319 or equivalent). The wafer is then placed in a physical vapor deposition (PVD) system where a metals are deposited during a metal deposition step 28. Example PVD systems include: sputtering, electron beam evaporation and pulsed laser
5 deposition. The metals deposited by the appropriate PVD system consist of an adhesion layer (such as Cr, Ta, or W) followed by the desired electrode material (such as Au, Ag, Cu or Pt). The thicknesses of these layers may vary substantially, but are typically 100-500 Å for the adhesion layer and 1000-5000 Å for the electrode layer. Following a lift-off step 30 to remove the excess metals, a second layer of photoresist is then deposited on
10 the wafer during a second photoresist deposition step 32, cured as described above, and photolyzed through an isolation mask 35 during a second photolysis step 34. The aim of this second photolysis step is to expose only the regions of the electrode pads 36 and an outer contact ring 38, the exposed photoresist on which is dissolved away after the photolysis step. A final annealing step 40 at between 90°C and 130°C for between 1
15 minute and 10 (or more) minutes hardens the remaining photoresist into an effective insulating layer. Alternately, an insulating layer (such as glass, silica, alumina, magnesium oxide, silicon nitride, boron nitride, yttrium oxide or titanium dioxide) may be deposited in place of the hardened photoresist by a suitable PVD technique after photolysis of the second photoresist layer through an inverse isolation mask (the negative
20 of the isolation mask 35 in Fig. 2C).

The arrays of the present invention consist of a plurality of individually addressable electrodes that are insulated from each other (by adequate spacing) and from the substrate (since they are fabricated on an insulating substrate), and whose interconnects are insulated from the electrochemical testing solution (by the hardened
25 photoresist or other suitable insulating material). The number of electrodes can vary according to a desired number, but typically the arrays consist of 10 or more electrodes, 30 or more electrodes, and preferably more than 50 electrodes. In the embodiments shown in Fig. 1A and Fig. 1B, more than 60 electrodes are in a single array. Materials are deposited on each of the individually addressable electrodes. Thus, an array of
30 individually addressable materials is also a part of this invention, with the number of

materials equaling the number of addressable electrodes. The materials in the array may be the same or different, as described below.

The deposition of materials on the above described electrode arrays to make a library of an equal number of compositions is accomplished by the electrodeposition of species from solution using standard electrochemical methods. The compositions may all be the same, or may be different from each other. In one embodiment of the present invention, the depositions are carried out by immersing the electrode array in a standard electrochemical deposition chamber containing the array, a platinum mesh counter electrode, and a reference electrode (e.g., Ag/AgCl). The chamber is filled with a plating solution containing known amounts of source materials to be deposited. By selecting a given electrode and applying a predetermined potential for a predetermined amount of time, a particular composition of materials (which may or may not correspond to the exact composition of the plating solution) is deposited on the electrode surface. Variations in the compositions deposited may be obtained either by directly changing the solution composition for each deposition or by using different electrochemical deposition techniques, or both. Examples of how one may change the electrode composition by changing the deposition technique can include: changing the deposition potential, changing the length of the deposition time, varying the counter anions, using different concentrations of each species, and even using different electrochemical deposition programs (e.g., potentiostatic oxidation/reduction, galvanostatic oxidation/reduction, potential square-wave voltammetry, potential stair-step voltammetry, etc.). Through repeated deposition steps, a variety of materials may be serially deposited on the array for the aforementioned library.

In an alternate embodiment of the present invention, the deposition of materials on the electrode array is carried out using a partially or fully automated solution delivery/electroplating system consisting of a deposition head and its associated syringe pumps, robotics and electronics. As illustrated in Fig. 3, the deposition head 50 consists of a rod 52 that is tapered at the tip. The tapered end of the deposition head is wrapped with a mesh counter electrode 54 (e.g., Pt) that is connected to an external power supply (not shown) via a wire 56 that is embedded in the wall of the head. In a preferred embodiment of the present invention, the deposition head has a 1-3 mm ID which is

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tapered to ca. 1 mm ID at the tip. A solution delivery tube 58 containing an interannular reference electrode 60 is located into the center of the rod 52. The reference electrode 60 may be a standard reference electrode (such as Ag/AgCl, SHE, SCE or Hg/HgSO₄) or a quasi-reference electrode (such as a piece of Pt wire). The reference electrode 60 is split
5 off from the solution delivery tube 58 and connected to an external power supply or potentiostat (not shown). The flow of liquids through the solution delivery tube 58 is controlled by commercially available syringe pumps (not shown) that can precisely deliver volumes of liquids with accurate displacements in the $\mu\text{L}/\text{hour}$ regime. Although any number of syringe pumps can be used, at least one is desirable and the exact number
10 of pumps will ultimately depend on the complexity of the desired depositions (i.e., binary = two pumps, ternary = three pumps, quaternary = four pumps, etc.). The liquids that are dispensed from the aforementioned pumps are either mixed prior to entering the solution delivery tube (via an external mixer) or via a frit 62 embedded in the deposition head. During the deposition process, the deposition head 50 is held over a given electrode pad
15 12 on an electrode array 10 by a clamp 68 that is connected to robotics (not shown) that can control its precise position. In a preferred embodiment of the present invention, the ideal position, as illustrated in Fig. 3, is ca. 1-2 mm above the electrode pad 12.

Still referring to Fig. 3, the operation of the automated deposition system is described as follows. After positioning the deposition head above a given electrode
20 (sometimes referred to as the 'working' electrode), the syringe pumps are activated causing a predetermined mixture of liquids containing predetermined amounts of source materials to flow through the tube 58 at an exactly specified flow rate and collect in a region 70 surrounding a given electrode 12. When the liquid contacts all three electrodes, a complete electric circuit is formed in this region. Coincident with the formation of this
25 circuit, a predetermined potential is applied to the working electrode (via an external power supply or potentiostat) causing species present in the liquid above it to deposit on the electrode surface. After a predetermined deposition time, the head is rinsed and moved to the next electrode where the next specified mixture is delivered and plated out. In a preferred embodiment of the present invention, a deposition time of between 1 and 2
30 minutes is used. The entire procedure can take less than 3 minutes per deposition or about three hours per library of sixty-four to sixty-six elements.

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The electrochemical cell used to measure properties of the materials deposited on the above described electrode arrays is illustrated in Figs. 4A-4E. Referring to Figs. 4A-4B, the cell 80 comprises a cylindrical glass housing 82 (of approximate diameter equal to that of the wafers) that is sandwiched between two plastic end members 84. The anode array assembly 86, which holds the individually addressable electrode arrays 10, is fit into one side of the cell, and the cathode assembly 95, which holds a counter electrode 88 and its associated external wire coupling 96, is fit into the other side. The cell is held together by four screw fasteners 90 which fit through holes 98 located on the corners of the end members 84. A reference electrode compartment 92 is bored into the glass housing to allow the insertion of a reference electrode (not shown). A liquid filling hole 94 allows for the filling and drainage of testing solutions from the electrochemical cell.

Referring to Fig. 4C, an exploded view of the components of the anode assembly is shown. The glass housing 82 of the cell is fit over the inner flange 106 of a molded adapter 102 and is held in place against the adapter with an o-ring 100. This o-ring provides a water-tight seal for this part of the assembly. The diameter of the outer flange 104 of the adapter 102 is the same as that of the glass housing, while that of the inner flange 106 is slightly smaller allowing one half of it to fit into the glass housing and the other half of it to fit into the remaining pieces of the anode assembly. A groove 108 is cut into the lower lip of the adapter 102. This groove holds an o-ring 110 which makes a water-tight seal with the anode array 10 when the adapter is pressed against it. Electrical contact to the anode array 10 is made using a ring of elastomeric contacts 114 which are pressed between the peripheral pads of the array (see Figs. 1A-1B) and contact pads 122 on a printed circuit board (PCB) assembly 112. These elastomeric contacts contain miniature wires encased in a flexible rubber sheath. They are commercially available and known to those skilled in the art. The anode array 10 is affixed to a backing plate 116 and attached to the PCB 112 with screws (not shown) through holes 118. This backing plate holds the electrode array and ensures contact between the peripheral pads on the wafer and the contacts on the PCB. This completes the anode assembly which is fitted together with screw fasteners 90 through holes 98 in end member 84 as shown in Fig. 4A.

Referring now to Figs. 4D-4E, the PCB 112 and its associated circuit diagram 130 are described as follows. The PCB 112 consists of a rectangular plate 120 on which is

deposited an intricate pattern of wires and connectors. The contact pads 122, which provide electrical connection to peripheral pads on the anode array (Figs. 1A-1B), are routed to four high-density pin connectors 128 that provide a cable connection to an external power supply (not shown) or multi-channel potentiostat 132. The multi-channel potentiostat 132 is essentially a collection of individual potentiostats bundled together in a single unit. These individual potentiostats can precisely control the current or potential applied to each electrode in the system. A common reference electrode contact 124 and a common counter electrode contact 126 are also wired to the high density pin connectors so that individual electrode pads on a given electrode array may be connected to the same reference and counter electrode during test measurements in the electrochemical cell.

Using the PCB 112 in conjunction with the deposition head 50 (Fig. 3) and the multi-channel potentiostat, each individual electrode on a given anode array can be individually addressed (e.g., during an electrodeposition procedure). Alternatively, using the PCB in connection with the electrochemical cell setup 80 (Fig. 4A) and multi-channel potentiostat, all of the electrodes on the array may be simultaneously addressed (e.g., during a catalytic activity measurement). Such catalytic measurements can be made in a time frame of between 1 and 2 minutes for each array of materials.

In the PCB illustrated in Fig. 4D, a sixty-four contact pad configuration is shown. It should be understood that a sixty-six contact pad configuration would be needed for experiments using a sixty-six member electrode array (Fig. 1B), and that PCB's having greater or less contact pads and associated connections are straightforward extensions of the concept and intended to be included within the scope of the present invention.

EXAMPLE

The following example illustrates the electrochemical deposition and screening measurements for a very specific system using selected embodiments of the present invention. It is only one of the many possible uses of the present invention. The example illustrates how a library of sixty-four different Pt-Ru compositions may be prepared and tested for methanol oxidation activity. It should be understood that the solution and

electrode compositions, types of reference and counter electrodes, applied and measured potentials, screening test conditions, and associated results are merely illustrative and that a person skilled in the art may make reasonable substitutions or modifications to these components without deviating from the spirit and scope of the invention.

5 A binary Pt-Ru library containing sixty-four different Pt-Ru compositions was synthesized on a sixty-four element individually addressable electrode array (gold electrodes) using the electrochemical reduction of acidic solutions containing mixtures of platinum chloride (H_2PtCl_6) and ruthenium chloride (RuCl_3). Starting with a stock solution of 150ml of 0.01M RuCl_3 (in 0.5M H_2SO_4) that was placed in a standard
10 electrochemical deposition chamber along with the electrode array, a Pt mesh counter electrode, and a silver/silver chloride (Ag/AgCl) reference electrode, the first working electrode on the array was held at a constant potential of -0.25V (vs Ag/AgCl) for two minutes under constant stirring. The electrode array was then rotated in the deposition chamber and the solution composition adjusted (by the removal of a 5ml aliquot of the
15 RuCl_3 solution and its replacement with a 5ml aliquot of a 0.01M H_2PtCl_6 solution), where the next electrode was deposited at the same potential and for the same amount of time. This procedure was continued until all sixty-four electrodes were deposited with Pt-Ru compositions, whose thickness averaged between 1000-2000 Å. Analysis (via X-ray fluorescence measurements) of the sixty-four electrodes showed a continuously
20 varying gradient of Ru and Pt compositions among the sixty-four electrodes on the array.

 This Pt-Ru library was then screened for methanol oxidation activity by placing it into the electrochemical cell (described earlier) which was filled with a solution of 1.0M methanol in 0.5M H_2SO_4 (a standard testing solution composition for studying the electrooxidation of methanol in fuel cells). The cell also contained a Hg/HgSO_4
25 reference electrode and a Pt mesh counter electrode. Chronoamperometry measurements (i.e., holding a given electrode at a given potential and measuring the current that passes as a function of time) were then performed on all of the electrodes in the library by pulsing each individual electrode to a potential of -0.125V (vs Hg/HgSO_4) and holding it

there for 1 minute while monitoring and recording the current that passed. The results of this experiment are depicted in Fig. 5.

Referring now to Fig. 5, a three-dimensional plot 140 of electrode composition 142 (expressed as mole fraction platinum) versus current 144 (in amps per square centimeter) versus time 146 (in seconds) is displayed. Individual electrodes are represented by their compositions along the x-axis, with their associated activities represented by their current values on the z-axis. The most active electrode compositions 150 are centered around a 50:50 Pt:Ru electrode composition which agrees with results reported in the literature (e.g., D. Chu and S. Gilman, *J. Electrochem. Soc.* **1996**, *143*, 1685). Although the results plotted in Fig. 5 correspond to a simple binary library of Pt-Ru compositions made by the serial deposition of Pt-Ru solutions in a standard deposition chamber and studied by serial chronoamperometry measurements made on a single channel potentiostat, the same depositions and measurements could be made in parallel with a multi-potentiostat using the deposition head and PCB interface of the present invention (Figs. 3 and 4D). In fact, significantly more complicated libraries using ternary, quaternary and greater compositions are possibly simply by changing the composition of the initial plating solutions. Plating solutions comprising one or more of the water soluble forms of the transition elements (e.g., Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg) as well as many main group elements (e.g., Al, Ga, Ge, In, Sn, Sb, Te, Tl, Pb, Bi) can be used with the present invention, and will give rise to enormous variations in library compositions which can in turn be studied in an enormous variety of catalytic systems.

As should now be readily apparent, the present invention provides a far superior method of electrochemically depositing and screening the properties of diverse materials. Using this invention, one can efficiently prepare libraries of varying elemental composition, and, since these libraries are prepared on individually addressable electrode arrays, one can also directly measure properties of these compositions. Using the present invention, it should be possible to synthesize and screen millions of new compositions at an unprecedented rate.

It is to be understood that the above description is intended to be illustrative and not restrictive. Many embodiments will be apparent to those of skill in the art upon reading the above description. The scope of the invention should, therefore, be determined not with reference to the above description, but should instead be determined
5 with reference to the appended claims, along with the full scope of equivalents to which such claims are entitled. The disclosures of all articles and references, including patent applications and publications, are incorporated herein by reference for all purposes.

What is claimed is:

1. A method of fabricating individually addressable electrode arrays, said method including the steps of:

providing an inert substrate;

5 applying photoresist to said substrate;

photolyzing preselected regions of said photoresist, said photolyzed regions being removable using a developer;

depositing one or more metals on said substrate;

removing predetermined regions of said metals, the remaining regions

10 forming said array of individually addressable electrodes.

2. The method of claim 1, wherein said step of photolyzing preselected regions of said photoresist includes the steps of:

placing an electrode mask over said wafer; and

15 exposing said wafer to ultraviolet light.

3. The method of claim 1, wherein said step of depositing one or more metals on said substrate comprises the deposition of an adhesion layer followed by the deposition of an electrode layer.

20

4. The method of claim 3, wherein said deposition of said adhesion layer comprises depositing between about 100 and 500 Å of a metal selected from the group consisting of Cr, Ta and W.

25 5. The method of claim 3, wherein said deposition of said electrode layer comprises depositing between about 1000 and 5000 Å of a metal selected from the group consisting of Au, Ag, Cu and Pt.

6. The method of claim 1, further comprising the step of depositing an
30 insulating coating on selected regions of said substrate.

7. The method of claim 6, wherein said step of depositing said insulating coating on selected regions of said substrate includes the steps of:

applying a second layer of photoresist to said inert substrate;

photolyzing preselected regions of said photoresist, the remaining regions

5 being removable using a developer; and

annealing said substrate for a predetermined time at a predetermined temperature.

8. The method of claim 7, wherein said step of photolyzing preselected
10 regions of said photoresist includes the steps of:

placing an isolation mask over said wafer; and

exposing said wafer to ultraviolet light.

9. The method of claim 7, wherein said step of annealing said substrate
15 comprises heating said substrate at between about 90-130°C for between about 1-10 minutes.

10. An array of individually addressable electrodes on an inert substrate, said array consisting of:

20 a plurality of electrode pads;

a plurality of contact pads;

wires connecting said contact pads to said electrode pads; and

an insulating layer covering said wires and a predetermined portion of said contact pads.

25

11. The array of claim 10, wherein said electrode pads are located substantially in the center of said substrate and said contact pads are located around the peripheral edge of said substrate.

12. The array of claim 10, wherein said inert substrate is selected from the
30 group consisting of glass, quartz, sapphire, alumina, plastic and thermally treated silicon.

13. The array of claim 10, wherein said insulating layer is selected from the group consisting of glass, silica, alumina, magnesium oxide, silicon nitride, boron nitride, yttrium oxide, titanium dioxide, and hardened photoresist.

5

14. The array of claim 10, wherein said electrode pads, said contact pads, and said wires are fabricated from conducting materials.

15. The array of claim 14, wherein said conducting materials are
10 independently selected from the group consisting of gold, platinum, silver and copper.

16. The array of claim 10, wherein said plurality of electrode pads comprises at least 10 electrodes.

15 17. The array of claim 16, wherein said plurality of electrode pads comprises up to 100 electrodes.

18. The array of claim 10, wherein said electrode pads have a surface area of between 1 and 2 mm².

20

19. A method of depositing diverse materials on individually addressable electrode arrays, said method including the steps of:

providing an array of individually addressable electrodes, a power source, a reference electrode and a counter electrode;

25 delivering a mixture of source materials to predetermined locations on said array; and

depositing a predetermined composition of said source materials on a given electrode on said array.

30 20. The method of claim 19, wherein said step of delivering said mixture of said source materials includes the steps of:

positioning a deposition head over a given electrode on said array; and
activating a predetermined number of syringe pumps associated with said
deposition head, said activation delivering a predetermined composition of said source
materials to said predetermined locations on said array.

5

21. The method of claim 20, wherein said step of positioning said
deposition head over said given electrode is accomplished using robotics.

22. The method of claim 21, wherein said robotics position said deposition
10 head at a predetermined distance above said given electrode.

23. The method of claim 19 wherein said depositing step includes a step
selected from the group consisting of changing the deposition potential, changing the
length of the deposition time, varying the counter anions, using different concentrations
15 of said source materials, and selecting the appropriate electrochemical deposition
program.

24. The method of claim 23, wherein said electrochemical deposition
program is selected from the group consisting of potentiostatic reduction, potentiostatic
20 oxidation, galvanostatic reduction, galvanostatic oxidation, potential square-wave
voltammetry, and potential stair-step voltammetry.

25. An apparatus for depositing diverse materials onto an array of
individually addressable electrodes, said apparatus comprising:
25 a rod having a tapered end;
a solution delivery tube within said rod;
a reference electrode within said solution delivery tube;
a counter electrode attached to said rod;
means for controlling the composition and flow rate of liquids through
30 said solution delivery tube;

means for mixing said liquids before said liquids exit said solution
delivery tube; and

means for controlling the position of said apparatus over said array.

5 26. The apparatus of claim 25, wherein said means for controlling the
composition and flow rate of said liquids through said solution delivery tube comprises at
least one syringe pump.

10 27. The apparatus of claim 25, wherein said means for mixing said liquids
before said liquids exit said solution delivery tube comprises an external mixer.

15 28. The apparatus of claim 25, wherein said means for mixing said liquids
before said liquids exit said solution delivery tube comprises a frit, said frit embedded in
said rod.

29. The apparatus of claim 25, wherein said means for controlling the
position of said apparatus over said array comprises robotics.

20 30. A system for electrochemically screening an array of materials, said
system comprising:
 an array of materials having an individually addressable electrode for each
material in the array; and
 means associated with each of said electrodes for simultaneously testing
each of said materials for said specific material property.

25 31. The system of claim 30, wherein said means comprises an
electrochemical cell, a multi-channel potentiostat, and a printed circuit board assembly.

30 32. The system of claim 31, wherein said electrochemical cell comprises:
a cylindrical glass housing, said housing sandwiched between two end
members and held in place with at least four screw fasteners;

5 a reference electrode compartment;
a liquid filling hole;
a cathode assembly; and
an anode array assembly, said anode array assembly holding said array of
individually addressable electrodes.

10 33. The system of claim 32, wherein said anode array assembly comprises:
a first o-ring, said first o-ring forming a water-tight seal with said glass
housing;
a molded adapter having an inner flange, an outer flange, and at least one
groove;
an array of individually addressable electrodes;
a second o-ring, said second o-ring fitting into said groove and forming a
water-tight seal with said array of individually addressable electrodes;
15 a printed circuit board;
a ring of elastomeric contacts, said elastomeric contacts located between
said array and said printed circuit board; and
a backing plate.

20 34. The system of claim 33, wherein said printed circuit board comprises:
a predetermined number of contact pads, said number of contact pads
corresponding to the number of individually addressable electrodes on said array;
at least four high density pin connectors;
a common reference electrode contact; and
25 a common counter electrode contact.

35. A method of testing a specific property of a material, said method
including the steps of:
depositing distinct materials on an array of individually addressable
30 electrodes;
placing said array in an electrochemical cell; and

screening said array for said specific property.

36. The method of claim 35, wherein said screening comprises:

pulsing all of said electrodes on said array to a predetermined potential

5 and monitoring and recording the current that is passed.

37. The method of claim 35, wherein said specific property for said array

is screened in a time frame of less than 5 minutes.

ABSTRACT OF THE DISCLOSURE

An electrochemical deposition and testing system consisting of individually
5 addressable electrode arrays, a fully automated deposition head, and a parallel screening
apparatus is described. The system is capable of synthesizing and screening millions of
new compositions at an unprecedented rate.

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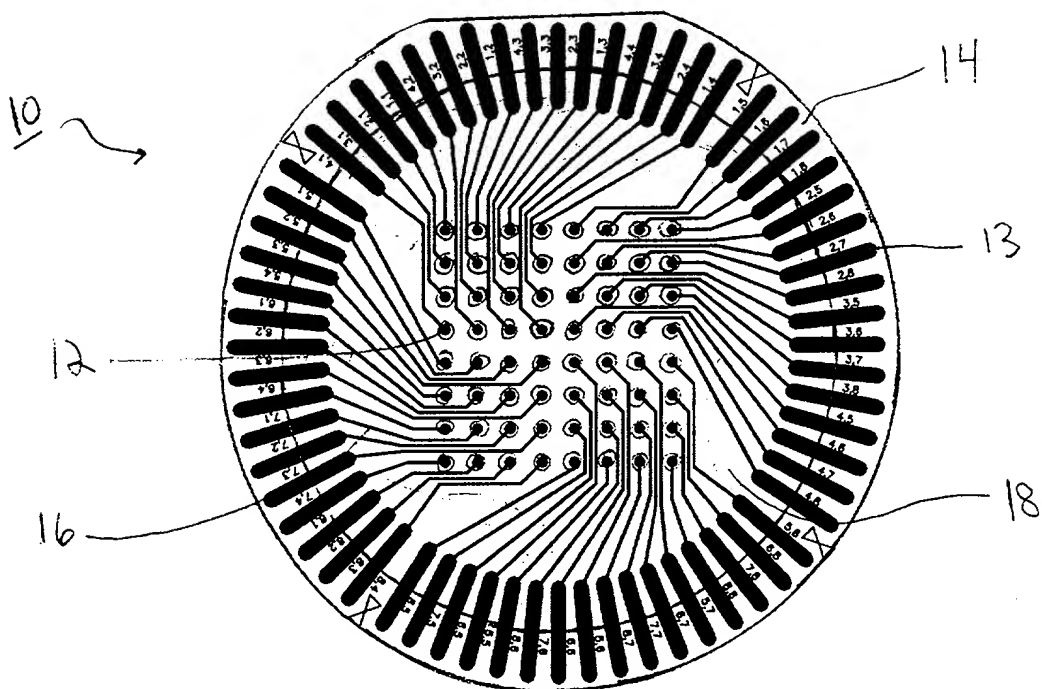


FIG 1 A

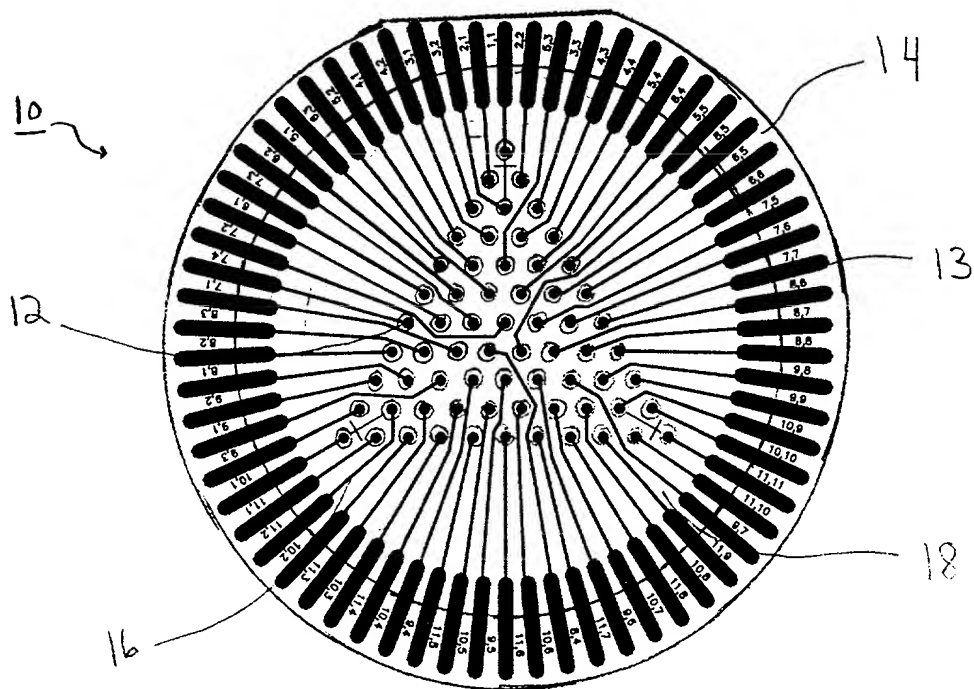


FIG 1 B

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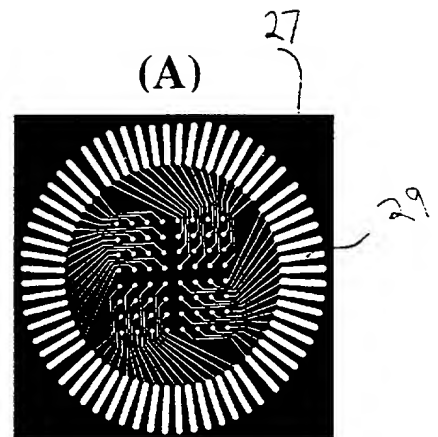
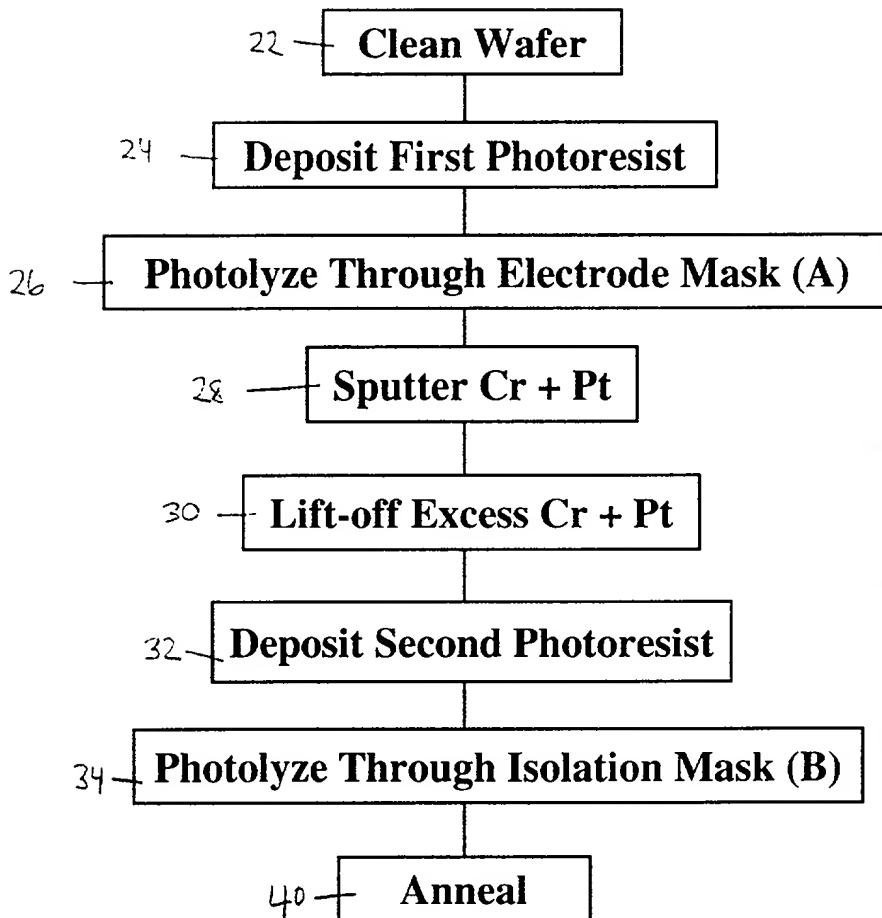


FIG 2B

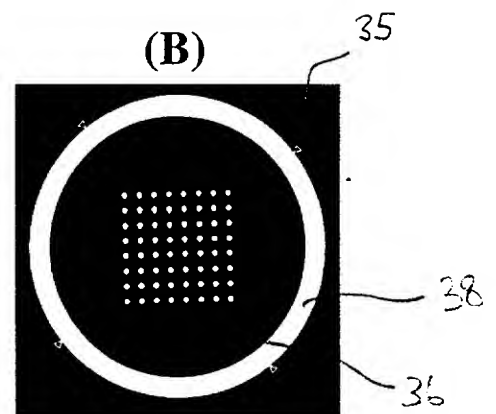


FIG 2C

FIG 2

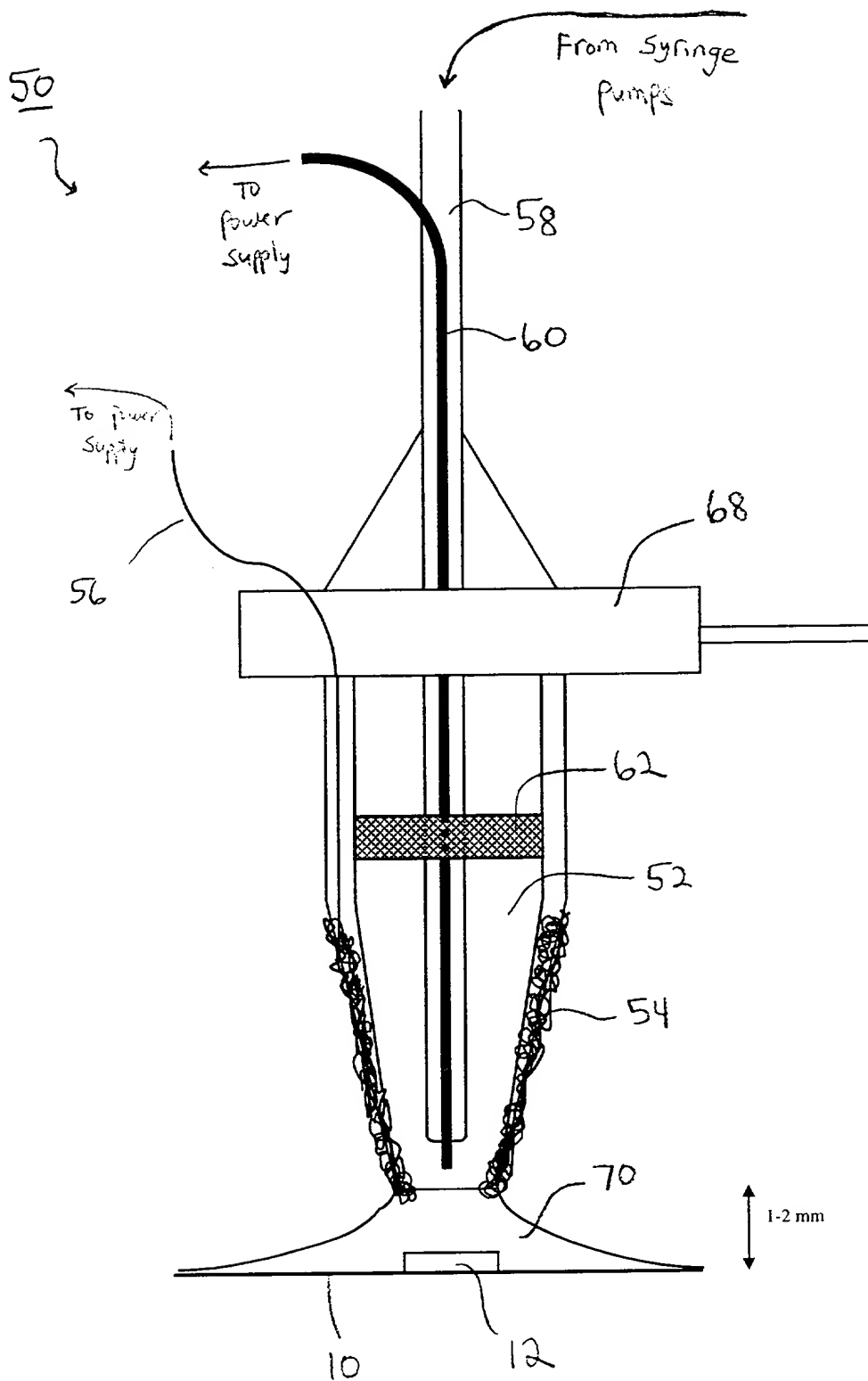


FIG 3

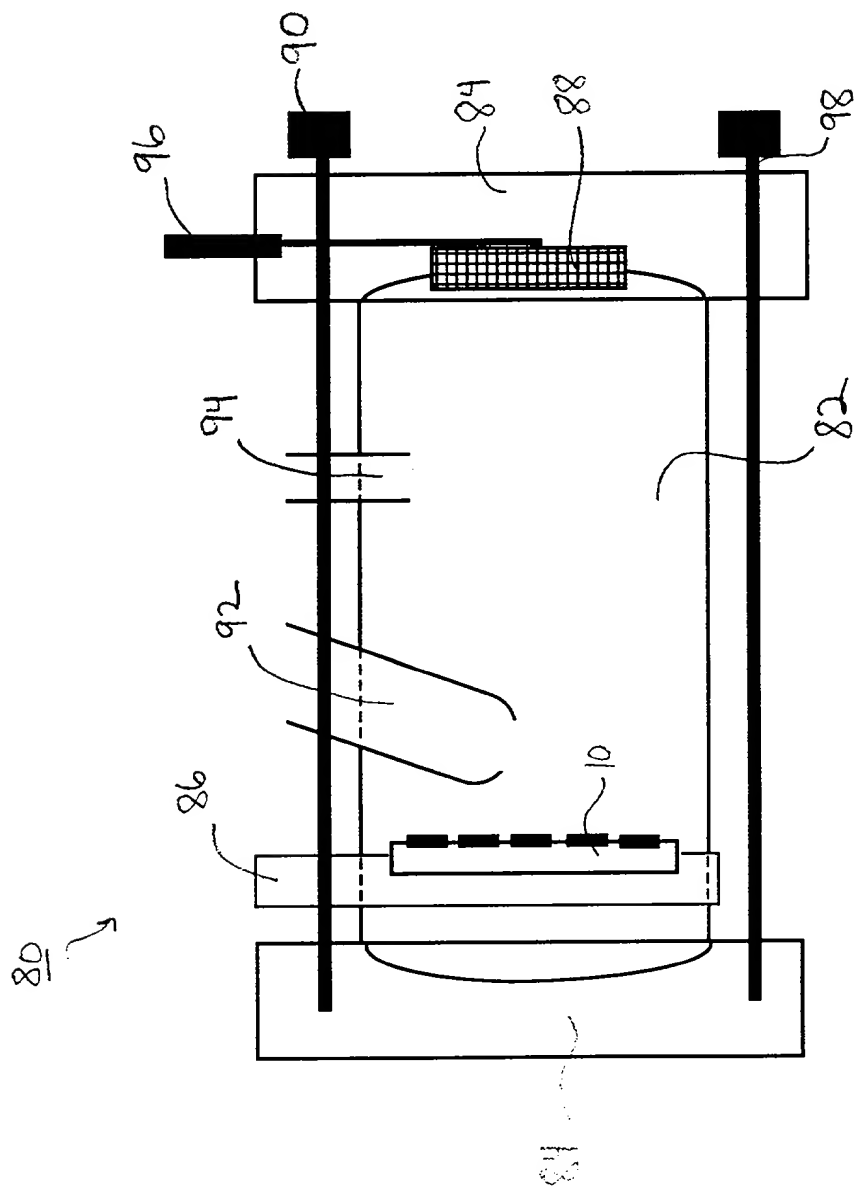
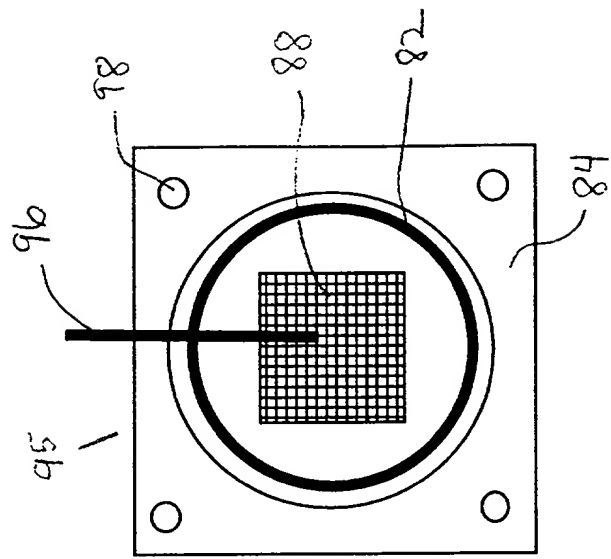


FIG. 4B



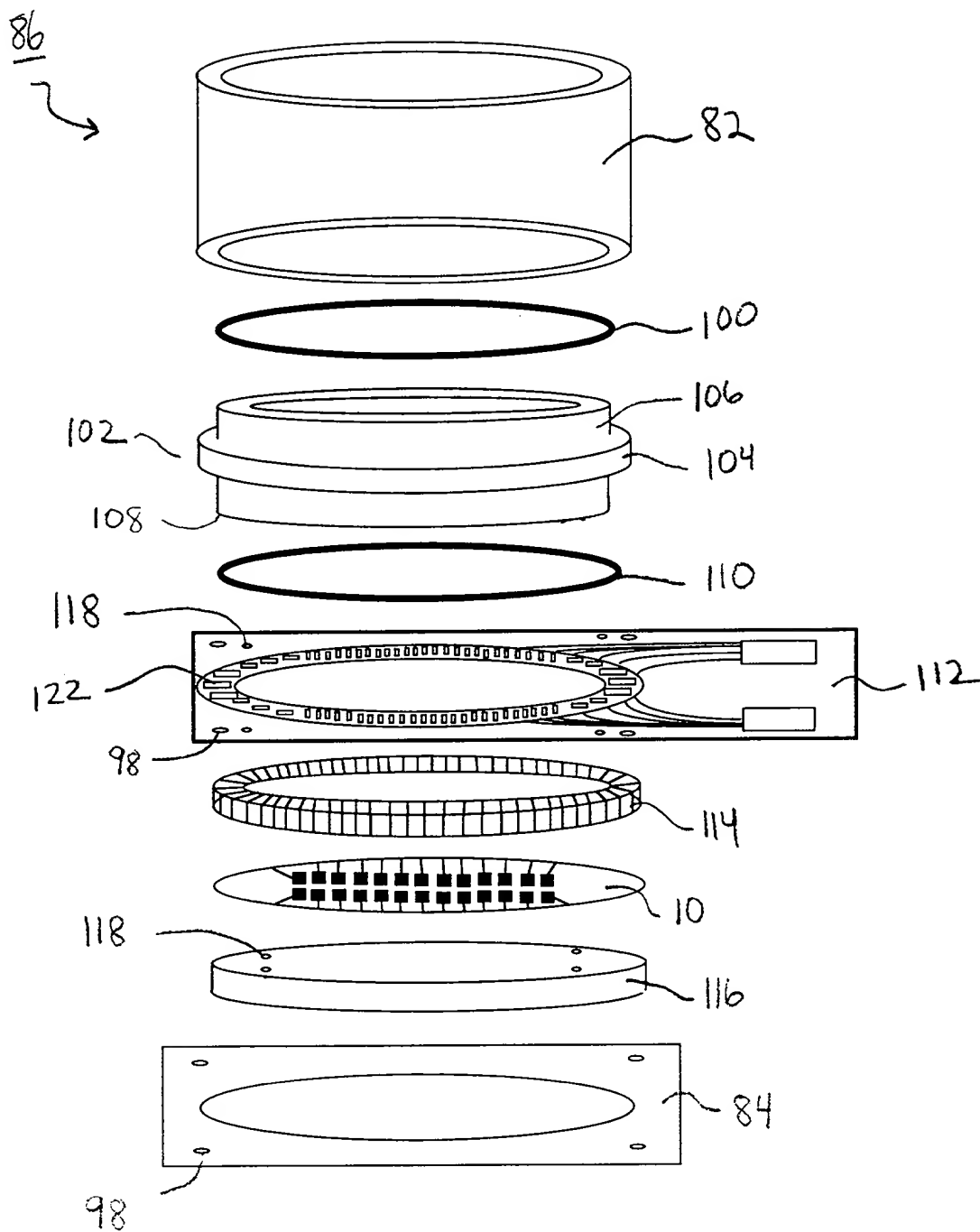


FIG 4C

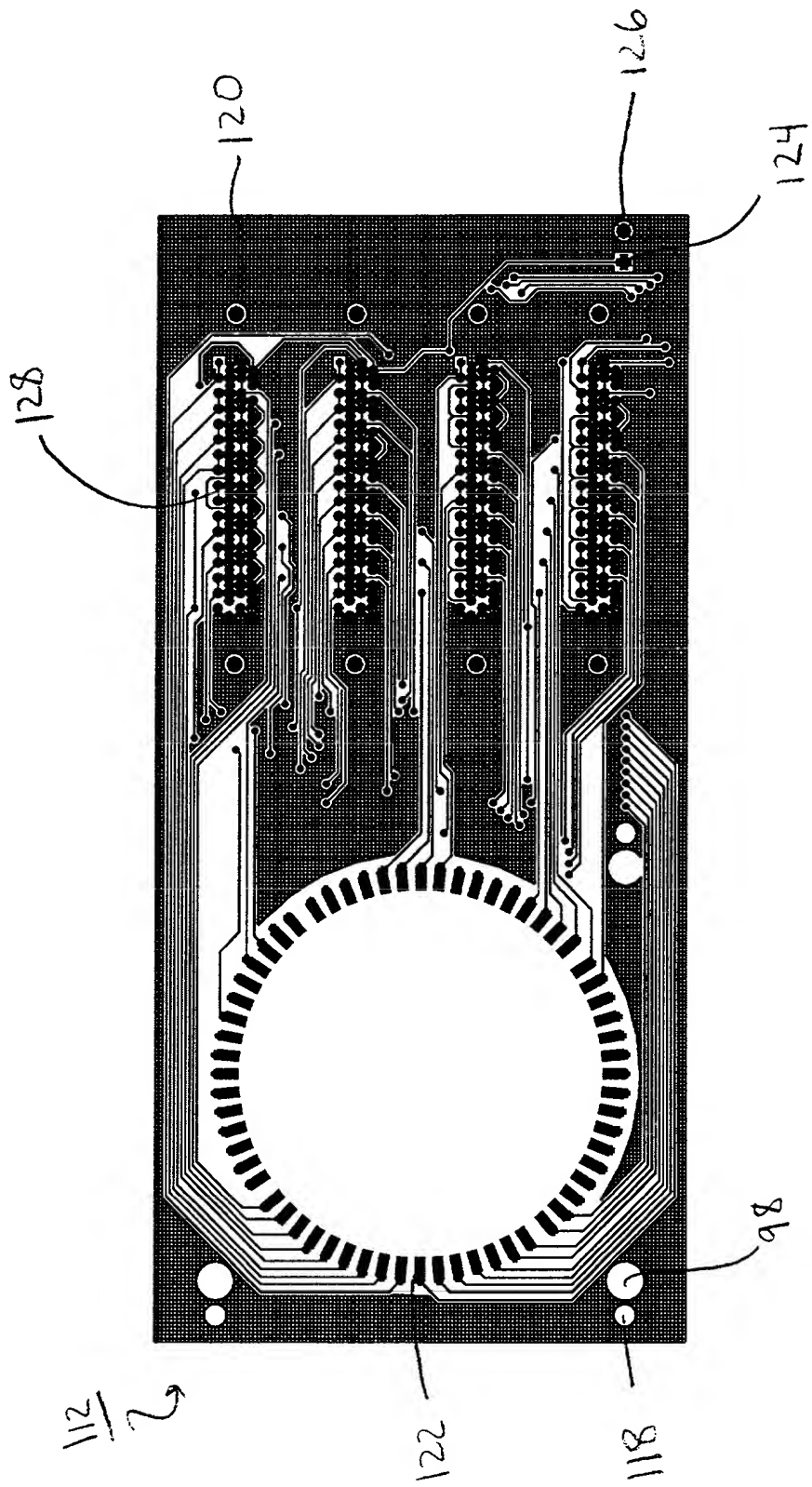


FIG. 4D

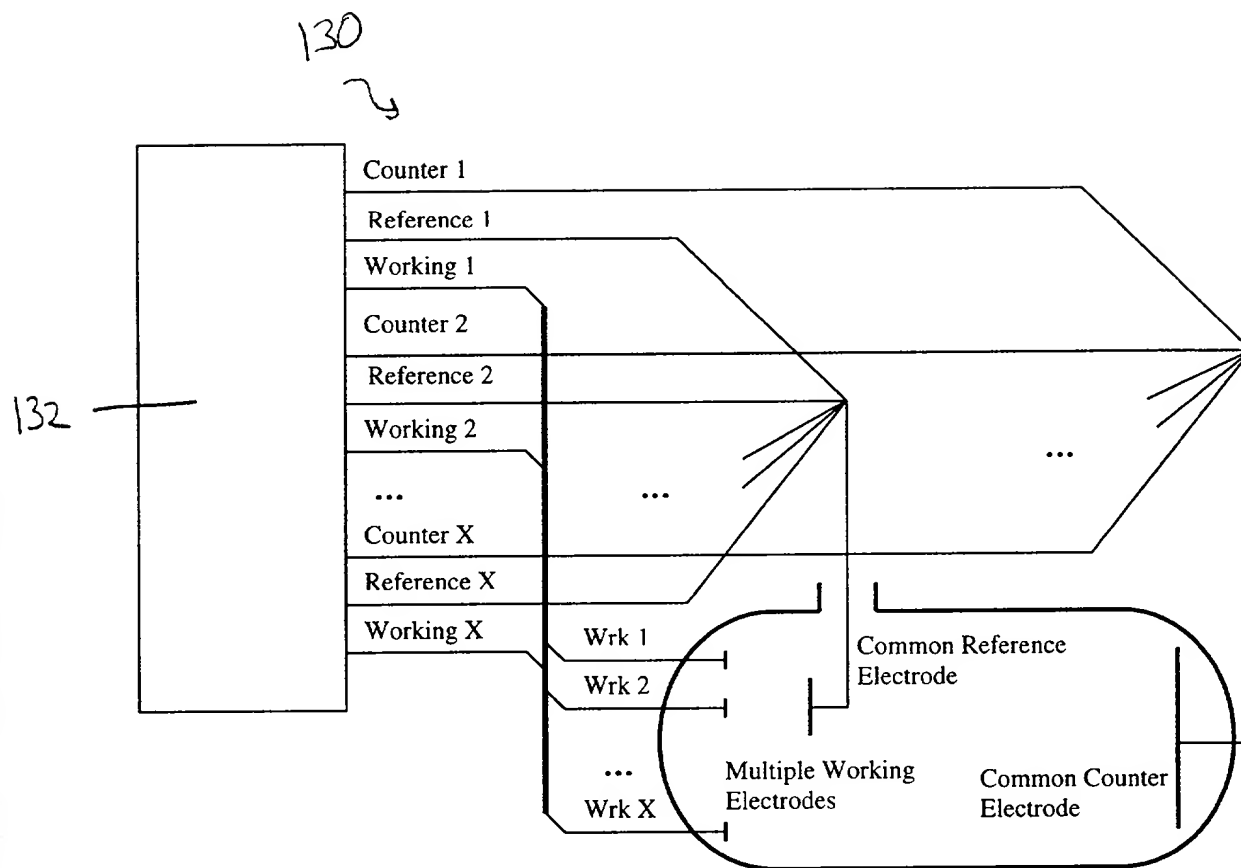
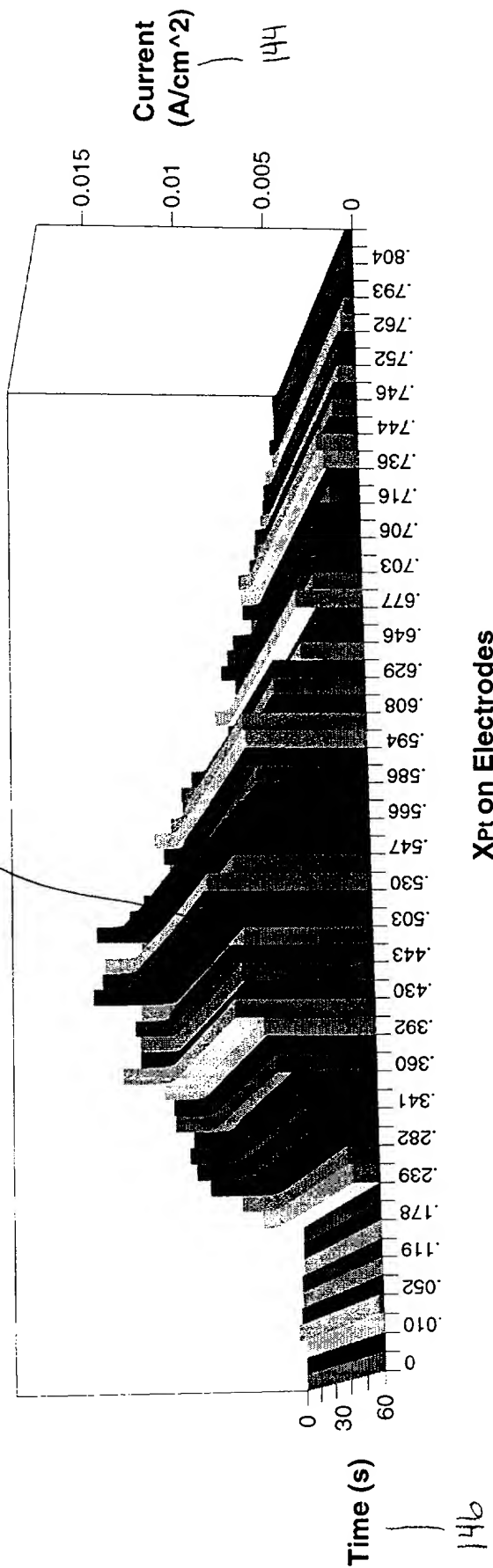


FIG 4E

140

150



XPt on Electrodes

142

FIG 5

DECLARATION

As a below and named inventor, I declare that:

My residence, post office address and citizenship are as stated below next to my name; I believe I am the original, first and joint inventor of the subject matter which is claimed and for which a patent is sought on the invention entitled: COMBINATORIAL ELECTROCHEMICAL DEPOSITION AND TESTING SYSTEM the specification of which ☒ is attached hereto or ☐ was filed on _____ as Application No. _____ and was amended on _____ (if applicable).

I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above. I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, Section 1.56. I claim foreign priority benefits under Title 35, United States Code, Section 119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed.

Prior Foreign Application(s)

Country	Application No.	Date of Filing	Priority Claimed Under 35 USC 119
			Yes <input type="checkbox"/> No <input type="checkbox"/>
			Yes <input type="checkbox"/> No <input type="checkbox"/>

I hereby claim the benefit under Title 35, United States Code § 119(e) of any United States provisional application(s) listed below:

Application No.	Filing Date

I claim the benefit under Title 35, United States Code, Section 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, Section 112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, Section 1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

Application No.	Date of Filing	Status
08/941,170	September 30, 1997	<input type="checkbox"/> Patented <input checked="" type="checkbox"/> Pending <input type="checkbox"/> Abandoned
		<input type="checkbox"/> Patented <input type="checkbox"/> Pending <input type="checkbox"/> Abandoned

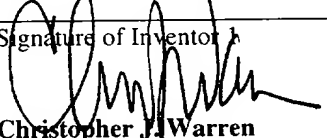
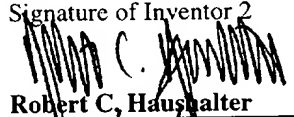
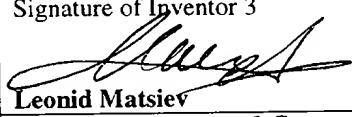
Power of Attorney: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith:

Ronald A. Krasnow, Reg. No. 33,321

20021022 16:23:00

Full Name of Inventor 1	Last Name Warren	First Name Christopher	Middle Name or Initial J.	
Residence & Citizenship	City Mountain View	State/Foreign Country California	Country of Citizenship United States	
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Full Name of Inventor 2	Last Name Haushalter	First Name Robert	Middle Name or Initial C.	
Residence & Citizenship	City Los Gatos	State/Foreign Country California	Country of Citizenship United States	
Post Office Address	Post Office Address 25259 Terrace Grove Road	City Los Gatos	State/Country California	Zip Code 95033
Full Name of Inventor 3	Last Name Matsiev	First Name Leonid	Middle Name or Initial	
Residence & Citizenship	City Cupertino	State/Foreign Country California	Country of Citizenship Russia	
Post Office Address	Post Office Address 10350 Leola Court, #1	City Cupertino	State/Country California	Zip Code 95014

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signature of Inventor 1 	Signature of Inventor 2 	Signature of Inventor 3 
Christopher J. Warren	Robert C. Haushalter	Leonid Matsiev
Date 7/16/98	Date 7/20/98	Date 07.16.98

00119187-072098

Express Mail Label No. EI768182393US

Attorney Docket No. 98-15

POWER OF ATTORNEY BY ASSIGNEE

SYMYX TECHNOLOGIES is the Assignee of the invention entitled:
COMBINATORIAL ELECTROCHEMICAL DEPOSITION AND TESTING SYSTEM,
the specification of which x is attached hereto or ____ was filed on _____
as Application Serial No. _____.

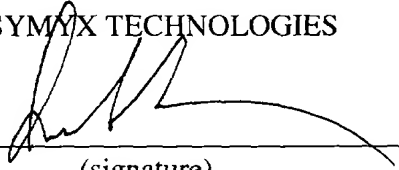
Assignee hereby appoints the following attorney(s) and/or agent(s) to prosecute
this application and transact all business in the Patent and Trademark Office connected
therewith.

Ronald A. Krasnow, Reg. No. 33,321

Send Correspondence to:	Direct Telephone Calls to: (Name, Reg. No., Tel. No.)
Ronald A. Krasnow Symyx Technologies 3100 Central Expressway Santa Clara, CA 95051	Ronald A. Krasnow Reg. No.: 33,321 (408) 330-2120

SYMYX TECHNOLOGIES

Date: 7/20/98

By: 
(signature)

Name: Isy Goldwasser
Title: President

050220 2097760

VERIFIED STATEMENT (DECLARATION) CLAIMING SMALL ENTITY STATUS
(37 CFR 1.9(f) & 1.27(c)) - SMALL BUSINESS CONCERN

Applicant or Patentee: Christopher J. Warren, Robert C. Haushalter and Leonid Matsiev

Application or Patent No.: _____

Filed or Issued: Even Date HerewithTitle: COMBINATORIAL ELECTROCHEMICAL DEPOSITION AND TESTING SYSTEM

I hereby declare that I am an official of the small business concern empowered to act on behalf of the concern identified below:

NAME OF SMALL BUSINESS CONCERN Symyx Technologies
ADDRESS OF SMALL BUSINESS CONCERN 3100 Central Expressway
Santa Clara, California 95051

I hereby declare that the above-identified small business concern qualifies as a small business concern as defined in 13 CFR 121.12, and reproduced in 37 CFR 1.9(d), for purposes of paying reduced fees to the United States Patent and Trademark Office, in that the number of employees of the concern, including those of its affiliates, does not exceed 500 persons. For purposes of this statement, (1) the number of employees of the business concern is the average over the previous fiscal year of the concern of the persons employed on a full-time, part-time or temporary basis during each of the pay periods of the fiscal year, and (2) concerns are affiliates of each other when either, directly or indirectly, one concern controls or has the power to control the other, or a third party or parties controls or has the power to control both.

I hereby declare the rights under contract or law have been conveyed to and remain with the small business concern identified above with regard to the invention, entitled COMBINATORIAL ELECTROCHEMICAL DEPOSITION AND TESTING SYSTEM by inventors Christopher J. Warren, Robert C. Haushalter and Leonid Matsiev described in

☒ the specification filed herewith
☐ Application No. _____, filed _____
☐ Patent No. _____, issued _____

If the rights held by the above identified small business concern are not exclusive, each individual, concern or organization having rights in the invention is listed below* and no rights to the invention are held by any person, other than the inventor, who would not qualify as an independent inventor under 37 CFR 1.9(c) if that person made the invention, or by any concern that would not qualify as a small business concern under CFR 1.9(d), or a nonprofit organization under 37 CFR 1.9(e).

*NOTE: Separate verified statements are required for each named person, concern or organization having rights to the invention averring to their status as small entities. (37 CFR 1.27)

Name: _____

Address: _____
☐ Individual ☒ Small Business Concern ☐ Nonprofit Organization

I acknowledge the duty to file, in this application or patent, notification of any change in status resulting in loss of entitlement to small entity status prior to paying, or at the time of paying, the earliest of the issue fee or any maintenance fee due after the date on which status as a small entity is no longer appropriate. (37 CFR 1.28(b)).

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application, any patent issuing thereon, or any patent to which this verified statement is directed.

NAME OF PERSON SIGNING
TITLE
ADDRESS OF PERSON SIGNING

Isy Goldwasser
President

Symyx Technologies
3100 Central Expressway
Santa Clara, California 95051

SIGNATURE  DATE 5/20/98

CERTIFICATE UNDER 37 C.F.R. § 3.73(b)Applicant: Christopher J. Warren, Robert C. Haushalter and Leonid MatsievApplication No.: _____ Filed: Even Date HerewithFor: COMBINATORIAL ELECTROCHEMICAL DEPOSITION AND TESTING SYSTEMSymyx Technologies

(Name of Assignee)

, a corporation

(Type of Assignee, e.g. corporation, partnership, university, government agency, etc.)

certifies that it is the assignee of the entire right, title and interest in the patent application identified above by virtue of either:

- A. ☒ An assignment from the inventor(s) of the patent application identified above. The assignment was recorded in the Patent and Trademark Office at Reel _____, Frame(s) _____, or for which a copy thereof is attached.

OR

- B. ☐ A chain of title from the inventor(s), of the patent application identified above, to the current assignee as shown below:

1. From: _____ To: _____
The document was recorded in the Patent and Trademark Office at
Reel _____, Frame _____, or for which a copy thereof is attached.
2. From: _____ To: _____
The document was recorded in the Patent and Trademark Office at
Reel _____, Frame _____, or for which a copy thereof is attached.

☐ Additional documents in the chain of title are listed on a supplemental sheet.

☐ Copies of assignments or other documents in the chain of title are attached.

The undersigned has reviewed all the documents in the chain of title of the patent application identified above and, to the best of the undersigned's knowledge and belief, title is in the assignee identified above.

The undersigned (whose title is supplied below) is empowered to act on behalf of the assignee.

I hereby declare that all statements made herein of my own knowledge are true, and that all statements made on information and belief are believed to be true; and further, that these statements are made with the knowledge that willful false statements, and the like so made, are punishable by fine or imprisonment, or both, under Section 1001, Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

DATE:

July 20, 1998

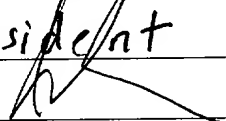
NAME:

Isy Goldwasser

TITLE:

President

SIGNATURE:

5/20/98

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